

Arctic chlorine monoxide observations during spring 1993 over Thule, Greenland, and implications for ozone depletion

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Abstract. We have determined the vertical distribution of chlorine monoxide (ClO), from measurements of pressure-broadened molecular-emission spectra made over Thule, Greenland, during the 1993 Arctic spring. The measurements show a weak lower stratospheric layer of chlorine monoxide inside the vortex in late February, which was, however, significantly greater in mixing ratio than that seen in observations we made in the spring of 1992. ClO was also observed in much smaller quantities in early to mid-March 1993 when Thule was outside the vortex. The amount of ClO within the vortex was severely reduced by the time it returned over Thule in late March. This reduction occurred several weeks earlier relative to the winter solstice than the decline of ClO inside the Antarctic vortex in 1993. The enhanced Arctic lower stratospheric layer seen in late February 1993 had a peak mixing ratio of about 0.5 parts per billion by volume (ppbv), slightly less than a factor of 3 smaller than that observed in the Antarctic in 1993 at a nearly equivalent photochemical period, and beyond. We have calculated daily ozone loss rates, due primarily to the dimer chlorine catalytic cycle, from both sets of measurements. The vertical integral of the Arctic daily percentage ozone loss when the largest ClO levels were present, at the end of February, is found to be approximately one quarter of that in the Antarctic at a photochemical period only 1 week later. The relative weakness of daily ozone depletion, combined with the early disappearance of ClO in the Arctic, suggests that hemispheric dilution by ozone-poor air from within the Arctic vortex is unlikely to be sufficient to explain the historically extreme loss of midlatitude northern hemisphere ozone which began in 1992 and persisted throughout 1993.

Introduction

Observations of depleted levels of ozone both within the Arctic vortex and at midlatitudes over populated areas [e.g., *Stolarski et al.*, 1991; *Komhyr et al.*, 1994; *Planet et al.*, 1994] have led to an increased effort to quantify the stratospheric chemical processing and ensuing ozone destruction taking place in the northern hemisphere. The primary mechanism which depletes the ozone layer inside the polar vortex is the ClO dimer catalytic cycle [*Solomon et al.*, 1990]. Ozone loss rates due to this catalytic cycle can be derived from measurements of the concentration of ClO, combined with

calculations of the rates of dimer formation, dissociation, and photolysis. Enhanced ClO mixing ratios were observed in the 1992 Arctic spring by the Upper Atmospheric Research Satellite (UARS) [*Waters et al.*, 1993], aircraft [e.g., *Toohey et al.*, 1993], and ground-based [*de Zafra et al.*, 1994b] instruments. We report here on new measurements of enhanced ClO in the 1993 Arctic spring, both inside and outside the polar vortex. We use the largest of these measurements to determine a single-day percentage ozone loss within the vortex, which we contrast with that found in the Antarctic at a similar photochemical period. We then comment on total ozone losses inside the two vortices over longer periods, based on solar exposure and the duration of the period in which chlorine remains in active forms capable of ozone depletion.

Instrument and Data Analysis

A ground-based millimeter-wave spectrometer containing a superconducting detector for improved sensitivity [*de Zafra et al.*, 1994a] was operated at Thule, Greenland (76.3°N, 68.4°W), as in the spring of 1992

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[*de Zafra et al.*, 1994b], to observe emission line spectra of the $J = 15/2$ to $J = 13/2$ rotational transition of ClO at ~ 278.6 GHz. All data shown here are averaged over midday, defined as starting 4 hours after sunrise and ending 2 hours before sunset at 18 km altitude. To remove the emission signal of a nearby ozone line, nighttime spectra are subtracted from the midday signal, with the high-altitude (>30 km, hence limited pressure broadening) portion of the residual nighttime ClO signal removed and replaced with a segment fit to the curvature of the underlying ozone line wing. The resultant differenced spectrum represents the true midday upper stratospheric emission intensity and the difference between midday and nighttime lower stratospheric emission intensities. The presence of a large diurnal variation of lower stratospheric chlorine monoxide indicates that photolysis of the ClO dimer is taking place and therefore that there is ongoing catalytic destruction of ozone. (Diurnal cycling from ClONO₂ would involve a comparatively negligible amount of ClO in this range of altitude and solar zenith angle [see *Froidevaux et al.*, 1985], especially with the severe reduction of chlorine nitrate due to denoxification in the polar vortex stratosphere). To improve signal-to-noise ratios, data from three or four days were averaged together. As an example, the resulting spectrum for February 25 – 28, 1993, is shown in Figure 1, where it is contrasted with a similarly processed spectrum for September 4 – 7, 1993, taken over McMurdo Station, Antarctica, to be discussed below.

The spectra were deconvolved to obtain vertical mixing ratio profiles using a modified Chahine-Twomey al-

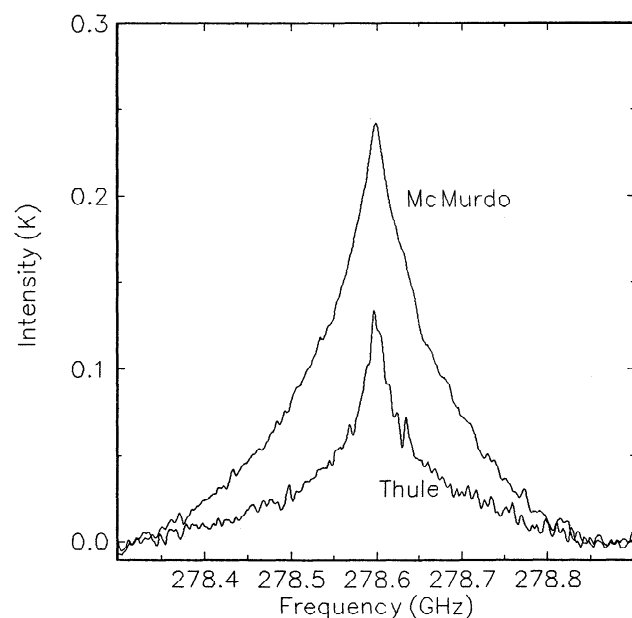


Figure 1. Spectra of the chlorine monoxide emission line at 278.6 GHz from February 25 – 28, 1993, over Thule, Greenland, and from September 4 – 7, 1993, over McMurdo Station, Antarctica. Intensity is shown in units of equivalent Rayleigh-Jeans radiation temperature. Data have been processed according to the method described in the text.

Table 1. Inversion Uncertainties

Source	Uncertainty, %
Deconvolutions	9.2
Retrieval method	5.3
Random noise	5.5
Inversion parameters	7.0
Instrument calibration	7.6
Sum in quadrature	15.8

Average contribution to uncertainty of retrieved February 24 – 28 midday mixing ratio for 17 – 21 km altitude. Uncertainties are 1σ values derived from each source, as discussed in the text. Inversion parameters include temperature, pressure, line strength, and pressure-broadening coefficient.

gorithm [*Twomey et al.*, 1977]. Deconvolutions were performed using several choices of starting profiles and weighting functions to minimize any biasing from a particular set of inputs, and the recovered profiles were averaged. Atmospheric pressure and temperature profiles used in the analysis were obtained from the National Meteorological Center (NMC) for appropriate dates and locations.

Uncertainties in addition to those from the data deconvolutions were established individually for each data set as follows. A noise-free spectrum was synthesized from the average of the recovered vertical profiles, then deconvolved using the same set of inputs referred to above to determine the accuracy of the retrieval method. Fifty random noise samples of the same magnitude as that seen in the original data spectrum were then added to the synthesized spectrum. These were deconvolved to measure the uncertainty due to the random noise inherent in our signal. The standard deviations of these results for each data set were added in quadrature with the standard deviations in retrieved mixing ratios determined for all data by studying the effects of changes in the temperature, pressure, line intensity, ClO broadening coefficient, and instrument calibration within their respective ranges of uncertainty. A detection limit of 0.05 ppbv was added to the final result. The overall 1σ uncertainty limits, including the detection limit, are indicated as a function of altitude by the horizontal bars in figures presented here. An example of the average contribution over 17 – 21 km altitude from each source of uncertainty is given in Table 1 for the February 25 – 28 retrieval.

Vertical Profiles

Vertical profiles of 1993 midday chlorine monoxide averaged over 3- to 4-day periods are shown in Figure 2. Both late February profiles show lower stratospheric (16 – 25 km) layers peaking at about 0.5 ppbv, distinctly enhanced with respect to the March profiles. The high-altitude (30 – 45 km) midday layer, which is not dependent on heterogeneous chemistry or the ClO dimer catalytic cycle, remains constant within error estimates during the entire series of measurements. It should be

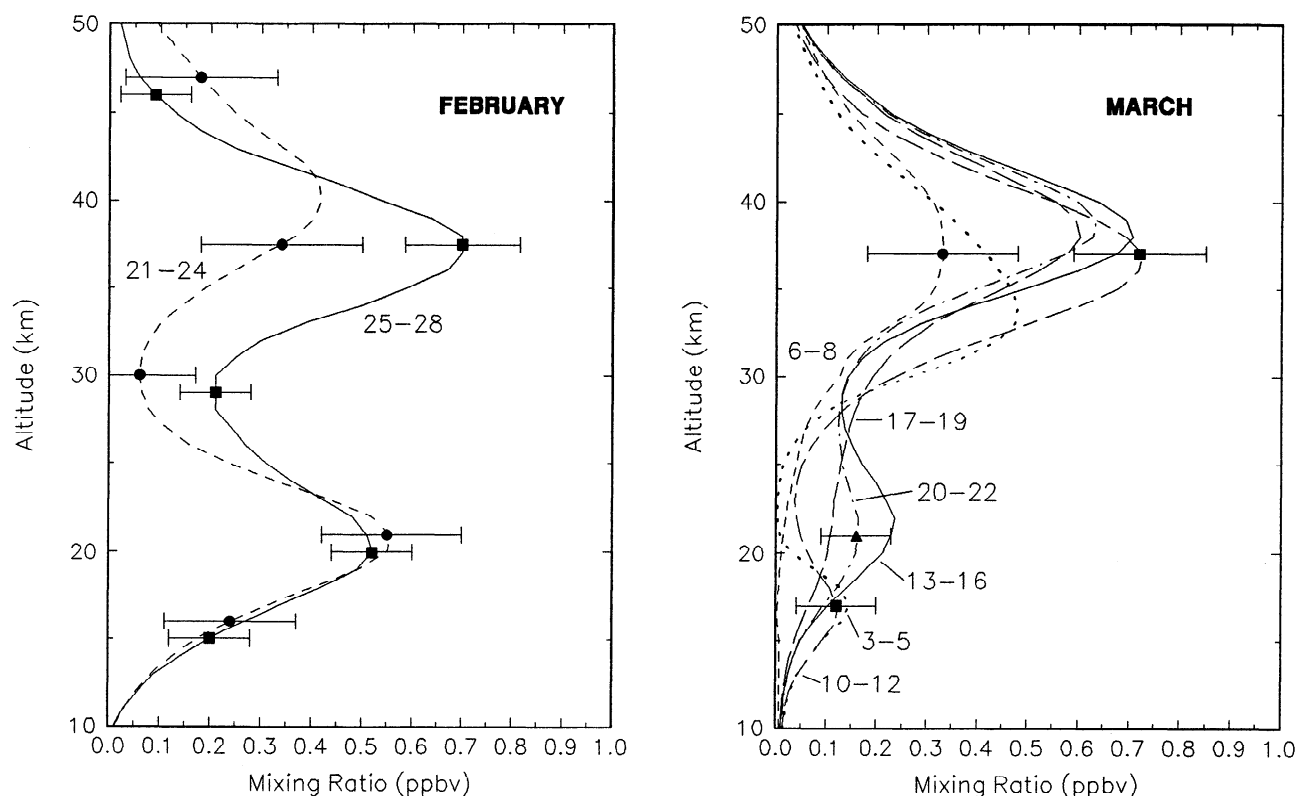


Figure 2. 1993 Thule midday ClO profiles. Data have been averaged over the indicated dates in each month. For clarity, only a few error bars, indicating the estimated total 1σ uncertainties (see text and Table 1), are shown at representative altitudes here and in the following figures.

noted that the February 21–24 and March 6–8 spectral data have signal-to-noise ratios roughly half those of other data. The February 21–24 data includes only 7 hours of observations, versus 14 hours for the February 25–28 data, due to a shorter midday and some instrumental difficulties during the earlier period. The March 6–8 data, due to bad weather, includes only 12 hours of observations, versus an average of 19 hours for other March data.

Correlations With Vortex Position

Potential vorticity and temperature maps from the European Centre for Medium-Range Weather Forecasts (ECMWF) and from the NMC have been used to determine the location of the edge of the Arctic vortex, defined as the location of the steepest gradients in potential vorticity on the 550 K potential temperature surface (~ 21 km altitude inside the vortex). Using this criterion, Thule was located inside or near the inner edge of the vortex during February 21–28 when the largest amounts of low-altitude ClO were observed. Thule was at the outer edge of the vortex on March 3, outside the boundary during March 4–13, again near the edge from March 14–17, and solidly back within the vortex during March 18–22. Gridded ECMWF temperatures for the Thule region correlate strongly with the motion of the vortex as defined above from potential vorticity. Temperatures were in the 198–208 K range while inside the vortex, rising to 223–238 K while outside

the vortex boundary. The edge periods of March 3 and March 14–17 both showed temperatures in the 218–223 K range, which dropped to 208–213 K during March 20–22 when the vortex had returned. This temperature pattern is also evident in local measurements from sondes launched at Thule by the Danish Meteorological Institute (P. Eriksen, private communication, 1993).

The mixing ratios shown in Figure 2 over Thule for measurements inside the vortex are in good agreement with large-area averages inside the vortex at ~ 20 km for ClO found by the UARS microwave limb sounder (MLS) during late February 1993 [Waters *et al.*, 1994].

We see that the lower stratospheric ClO layer within the February Arctic vortex was severely reduced by late March when the vortex again passed over Thule. Given the warmer temperature of this vortex air (see above), it is possible that HNO_3 had been released by this time from polar stratospheric cloud particles and photolyzed into OH and NO_2 . The latter would then have removed ClO by forming the reservoir species chlorine nitrate (ClONO_2).

Two of the three March profiles taken outside the vortex, those for March 3–5 and 10–12, indicate small ClO layers of ~ 0.1 ppbv between 16 and 18 km altitude. Ten-day back trajectories for March 5 and 10 indicate that the air at this altitude had been continuously outside the vortex, and thus the observed ClO probably did not result from heterogeneous chemistry

on polar stratospheric clouds (PSCs). We believe these slight layers may be evidence of extra-vortex processing on volcanic aerosols [e.g., *Rodriguez et al.*, 1994]. Lidar measurements from Thule on March 3 and 11 by the University of Rome (di Sarra, private communication, 1994) show aerosol-to-molecular backscatter ratios peaking above 2 at $\sim 13 - 14$ km, with the ratio still as high as 1.5 at 18 or 19 km, indicating an aerosol layer consistent with the altitude of our observed enhancement. The amounts of ClO we observed are similar to those seen in 1992 spring aircraft observations outside the polar vortex which showed ClO abundances between 0.05 and 0.12 ppbv [*Toohey et al.*, 1993]. The aircraft data were taken at 20 km, which should have sampled roughly the same aerosol as that which we see evidence of at a slightly lower altitude in 1993 spring, since the volcanic layer settled over time.

Comparison of 1992 With 1993 Arctic Spring

Chlorine monoxide measurements were also taken at Thule during the 1992 spring [*de Zafra et al.*, 1994b]. These measurements were made before several instrumental improvements were implemented and hence have larger uncertainties than those made in 1993. Figure 3 presents vertical profiles for February 25 – 28, when the vortex was over Thule in both years. The profiles show a nearly identical high-altitude ClO layer, but the abundances in the lower stratosphere were much lower

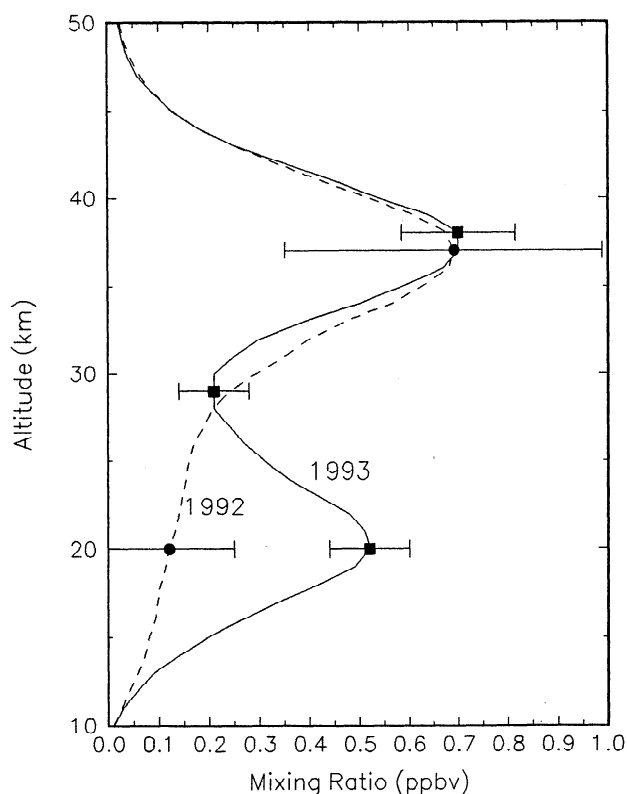


Figure 3. Thule midday ClO inside the polar vortex. February 25 – 28, 1993, contrasted with February 25 – 28, 1992. Error bars are as in Figure 2.

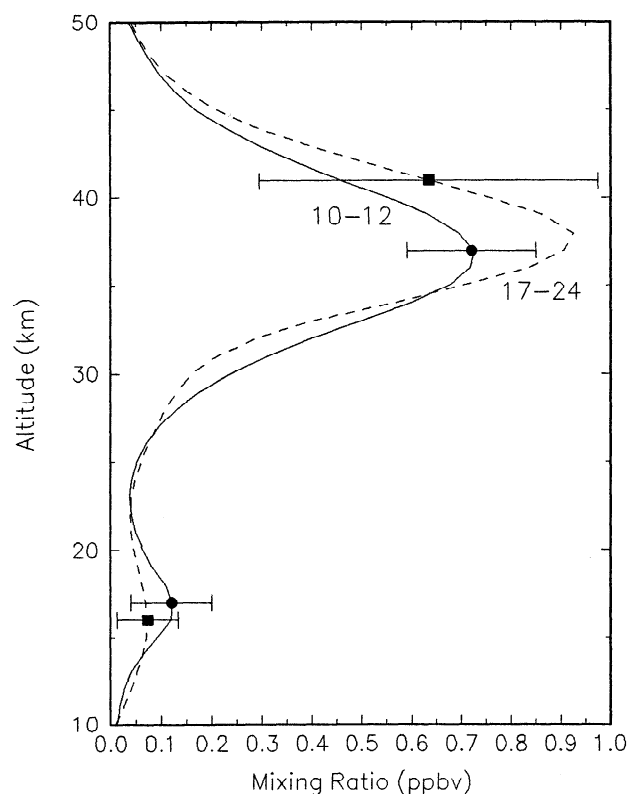


Figure 4. Thule midday ClO outside the polar vortex. March 10 – 12, 1993, compared with March 17 – 24, 1992. Error bars are as in Figure 2.

in 1992 than in 1993. This is again consistent with UARS/MLS findings for similar times in 1992 and 1993 [*Waters et al.*, 1994]. The 1992 profile shown here is a deconvolution of reprocessed data. The uncertainty at any altitude in the lower stratosphere is large, but all inversions show total column amounts of ClO below 30 km roughly equivalent to that shown here, which is significantly less than that seen in 1993.

The 1993 Arctic winter vortex was stronger than the 1992 (equivalent pressure surfaces descended to lower altitudes), was considerably colder, and most important, minimum temperatures remained below the threshold for PSC formation for several weeks longer than in 1992 [*Rosen et al.*, 1994]. The longer period of cold temperatures during the 1993 winter would allow for a longer period of heterogeneous chemical processing on PSCs to have taken place than in 1992, accounting for the greater observed ClO in 1993. In addition, delayed effects from Pinatubo aerosols may have enhanced the conversion of chlorine into active forms in 1993 relative to 1992 [*Rodriguez et al.*, 1994].

Figure 4 shows March data taken outside the vortex in both years. In this case, the 1992 and 1993 profiles are quite similar. Although the quality of the earlier data is comparatively poor, we observe that the 1992 data are not inconsistent with a similar but slightly smaller amount of extra-vortex ClO than was seen in 1993.

Comparison of Arctic and Antarctic Profiles

The same instrument was operated at McMurdo Station, Antarctica (77.9°S, 166.7°E), at nearly the same absolute latitude, during the 1992 and 1993 austral springs. The extent of heterogeneous chemical processing in the southern vortex is much greater than in the northern due to the prolonged colder temperatures and larger, more isolated vortex there. These conditions maintain most of the available chlorine in active forms, resulting in the severe destruction of ozone seen in the "ozone hole". Figure 5 contrasts 1993 midday chlorine monoxide profiles from within the polar vortices at the two locations. These profiles were obtained from the spectra shown in Figure 1. The mixing ratio at 20 km, approximately the peak of the lower layer, is slightly more than a factor of 3 greater in the Antarctic than in the Arctic. The profiles show a notable similarity in the altitudes of both layers and in the amount of chlorine present in the upper layer.

Ozone Depletion

The ozone loss rate due to the ClO dimer catalytic cycle, given that the rate-limiting step is the formation of the dimer, is given by

$$d[O_3]/dt = -2k_{\text{form}}[\text{ClO}]^2[M]\{J/(J + k_{\text{diss}}[M])\}$$

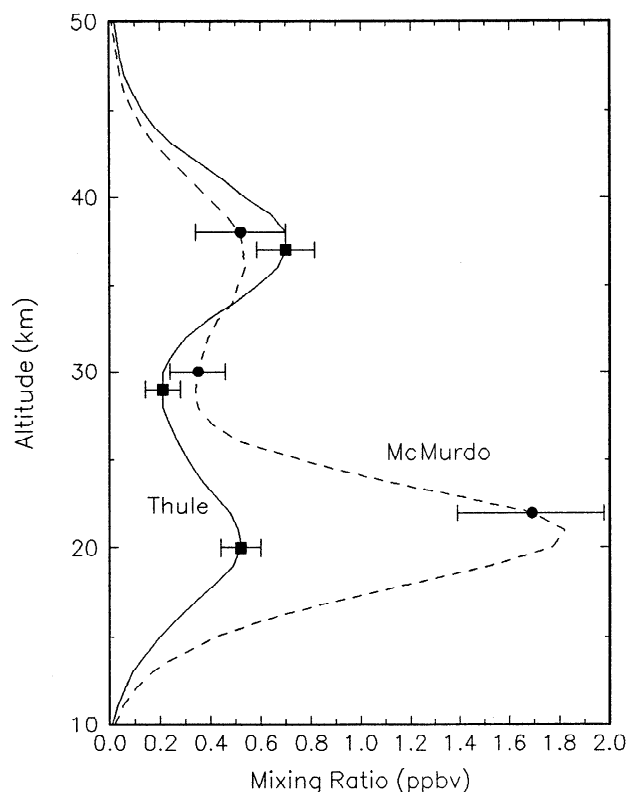


Figure 5. Arctic and Antarctic 1993 midday ClO profiles from within the polar vortex, February 25 – 28 and September 4 – 7 respectively. Error bars are as in Figure 2.

where $[O_3]$, $[ClO]$, and $[M]$ are the number densities of O_3 , ClO, and any third molecule; k_{form} and k_{diss} are the ClO dimer formation and dissociation rates; and J is the dimer photolysis rate. The term in braces represents the fraction of Cl_2O_2 destroyed by photolysis in contrast to thermal dissociation. That portion of the dimer which undergoes thermal dissociation adds to detectable ClO but does not lead to ozone destruction. Using a photochemical model, we derive the midday equilibrium dimer concentration from our ClO measurements and from calculated photolysis and chemical reaction rates. The model includes a small positive correction in the concentration of lower stratospheric midday ClO to account for subtraction of the residual nighttime amount. We then integrate the ozone loss in the model over 24 hours to arrive at a daily ozone loss rate. The loss rate depends primarily on the ClO dimer catalytic cycle but also includes a contribution from the BrO catalytic cycle which is $\sim 40\%$ that of the chlorine cycle in the Arctic but only $\sim 15\%$ in the Antarctic, using ~ 8 parts per trillion by volume bromine monoxide at 20 km in both cases [Toohey *et al.*, 1990, Brune *et al.*, 1989]. The difference arises because the ozone loss rate due to the bromine catalytic cycle depends on the product of the BrO and ClO concentrations, while that due to the ClO dimer catalytic cycle depends on the square of the ClO concentration. Therefore the larger amount of ClO in the Antarctic, with approximately the same amount of BrO, results in a larger contribution to ozone loss from the chlorine catalytic cycle relative to the bromine catalytic cycle. In the photochemical model we have taken reaction rates and photolysis cross sections from the 1992 NASA recommendations [DeMore *et al.*, 1992]. Photolysis rates were computed for a spherical atmosphere using a model incorporating the delta-Eddington method of calculating radiative transfer. This method is known to be accurate for the very high solar zenith angles at which the data were taken, given the high polar surface albedo [Dvortsov *et al.*, 1992; Briegleb, 1992]. Temperature and pressure profiles were from NMC data, while ozone concentrations used in the radiative transfer calculations were from the Thule balloon sondes and from sondes launched at McMurdo by the University of Wyoming (B. Johnson, private communication, 1993).

Figure 6 shows the daily percentage ozone loss rates as a function of altitude calculated from the Arctic and Antarctic ClO profiles shown in Figure 5 and local ozonesonde data for the appropriate dates. To facilitate comparison with similar calculations [e.g., Manney *et al.*, 1994], we show daily ozone loss in percent per day, although we believe it is more relevant to express the loss in absolute terms (e.g., in Dobson units per day). The Arctic loss rates were calculated for February 25 – 28, the period of greatest observed ClO enhancement. The Antarctic rates were calculated for September 4 – 7, the earliest data available, and therefore with the most similar photochemical conditions. Substantial loss rates are maintained at low altitudes where the ClO mixing ratio is dropping rapidly because this drop-off

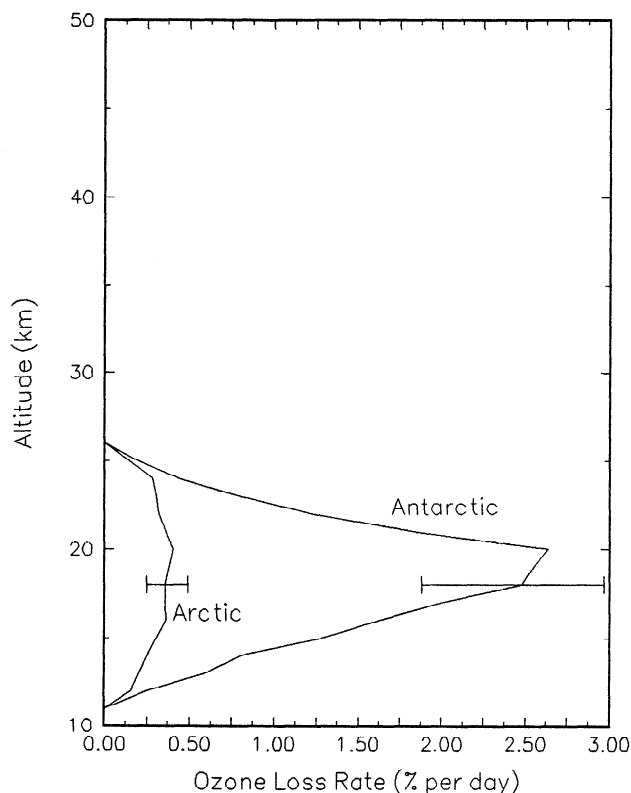


Figure 6. Daily Arctic and Antarctic ozone depletion rates calculated using the midday ClO concentrations in Figure 5, ~ 8 pptv BrO at 20 km, and local ozone sonde data. The error bars indicate the uncertainty in the loss rate due to the uncertainty in our ClO measurements only. The uncertainty contributed by uncertainties in the ClO dimer rate constants is much larger but affects each curve in a similar manner. The integral of the depletion rate over altitude in the Arctic is only 23% of that in the Antarctic.

is partly offset by the rapid rise in background pressure (see ozone loss rate equation). The vertical integral of the Arctic percentage loss rates is 23% of that in the Antarctic. The amount of ozone was greater over Thule however. The total column ozone loss rate in Dobson units (DU) was 0.7 DU per day over Thule, versus 1.9 DU per day over McMurdo. In terms of the total number of molecules of ozone destroyed per day, the Arctic rate was thus 37% of the Antarctic rate. The difference is primarily due to the quadratic dependence of the rate on the ClO concentration, with a smaller effect from the slightly longer period of solar exposure in the Antarctic (one week further after winter solstice).

The error bars shown in Figure 6 are those due to the uncertainty in our ClO measurements only. The uncertainty based on laboratory measurements of the rate constants, particularly the dimer formation rate, is much larger but would affect both of the curves in the same manner. This issue will be addressed quantitatively, and new limits will be set on the reaction rates, in a forthcoming paper comparing diurnal data with a photochemical model (Shindell, D. T., and R. L. de Zafra, Chlorine monoxide in the Antarctic spring

vortex over McMurdo Station, 1993 II: A comparison of measured and modelled diurnal cycling, submitted to *Journal of Geophysical Research*, 1993).

The total amount of ozone which is destroyed is of course dependent on the duration during which ozone destruction takes place and on the spatial extent of the destruction. In 1993, enhanced levels of ClO such as that shown in Figure 5 were already present in the Antarctic on September 4, the first day we acquired data, and persisted until the end of September. There were only 10 hours of sunlight at 18 km over Thule at the end of February, as compared with 16.5 hours at 18 km over McMurdo at the end of September. Thus the daily ozone loss rates calculated from our Antarctic measurements increased beyond that shown in Figure 6 throughout September, as chlorine remained in active forms and the duration of solar exposure increased.

ClO was also measured within the Arctic vortex during the mid-February to mid-March period of 1993 by the microwave limb sounder (MLS) aboard UARS [Waters *et al.*, 1994]. Estimates of the rate of ozone destruction based on these data have been made by Manney *et al.* [1994]. We compare here our data and calculated ozone loss rate with values presented by Waters *et al.* and Manney *et al.*, respectively. Waters *et al.* present vortex-averaged ClO in good agreement with the values and the temporal behavior that we observed at Thule. Manney *et al.*, using an earlier processing of UARS/MLS ClO data with slightly larger values, have calculated a vortex-averaged and time-averaged ozone loss rate of 0.9% per day at 20 km, including a contribution from the BrO cycle of $\sim 40\%$ of the ClO dimer cycle contribution. This is much larger than the ozone loss rate calculated here for the maximum mixing ratio at 20 km from our measurements of late February (which includes a similar contribution from bromine chemistry, based on our photochemical model).

We note that the loss rate calculated by Manney *et al.* is given as a vortex average for the entire mid-February to mid-March period. During this period the vortex-averaged ClO mixing ratio seen by the MLS [Waters *et al.*, 1994] exceeds 1 ppbv in early to mid-February, plummets to ~ 0.25 ppbv by the end of the month, and remains low throughout March. Because of the quadratic dependence on ClO concentration, the large early to mid-February ClO concentrations have an influence disproportionate to their duration. MLS vortex-wide data also include "hot spots" of ClO greater than 1 ppbv which likewise exert an influence disproportionate to their areal extent. The vortex-wide averaging as well as the time averaging are therefore likely to lead to a higher average ozone loss rate than the rate we calculate here for February 25 – 28 over Thule.

Summary and Conclusion

The daily creation of a lower stratospheric chlorine monoxide layer with a peak amplitude of about 0.5 ppbv at 20 km within the Arctic vortex was observed during late February 1993. Outside the vortex boundary in

March, this enhanced layer was not observed, but there was a small amount of ClO, perhaps resulting from heterogeneous processing on volcanic aerosols. Late March measurements, again within the vortex, show that the ClO layer had nearly disappeared, probably due to stratospheric renitrification during the first few weeks of March. The lower stratospheric layer clearly evident in 1993 was at the lower limit of detectability in 1992 at the same location under similar conditions. This observation is consistent with meteorological differences between the two winters and delayed effects from Pinatubo aerosols. Finally, we have compared a 1993 spring profile of enhanced chlorine monoxide from within the vortex over Thule with a 1993 spring profile taken within the Antarctic vortex over McMurdo Station at a similar latitude and photochemical period. Vertical integrals of daily percentage ozone loss rates calculated from the two profiles using a detailed radiative transfer calculation to derive photolysis rates show a loss rate over Thule only ~25% of the McMurdo loss rate, due primarily to the smaller observed ClO mixing ratios and greater ozone concentrations at Thule. In addition, the earlier disappearance of ClO within the Arctic vortex reduced the period of time when depletion chemistry was effective. Our results suggest that even with the unusually cold 1993 Arctic vortex and delayed chemical effects from Pinatubo aerosols, Arctic daily ozone loss through chlorine catalysis during the most active photolytic period was only a fraction of that seen over Antarctica 6 months later.

We note that the size of the Arctic vortex is roughly equivalent in area to that encompassed within the Arctic circle, or about 8% of the area of the northern hemisphere. Using either the ozone loss rate that we have calculated here from the maximum ClO mixing ratio observed by us over Thule or the value of the area- and time-averaged loss rate within the vortex calculated by Manney *et al.* [1994] from UARS ClO measurements, we believe that the significant northern hemispheric downtrend in ozone observed in 1993 [Komhyr *et al.*, 1994; Planet *et al.*, 1994] cannot be convincingly attributed to dilution from losses occurring only in the Arctic winter-spring vortex.

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References

- Briegleb, B. P., Delta-Eddington approximation for solar radiation in the NCAR community climate model, *J. Geophys. Res.*, **97**, 7603–7612, 1992.
- Brune, W. H., J. G. Anderson, and K. R. Chan, In situ observations of BrO over Antarctica: ER-2 aircraft results from 54°S to 72°S latitude, *J. Geophys. Res.*, **94**, 16639–16647, 1989.
- DeMore, W. B., S. P. Sander, C. J. Howard, A. R. Ravishankara, D. M. Golden, C. E. Kolb, R. F. Hampson, M. J. Kurylo, and M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, in *Evaluation 10*, *JPL Publ.* 92-20, 1992.
- de Zafra, R. L., W. H. Mallison, M. Jaramillo, J. M. Reeves, L. K. Emmons, and D. T. Shindell, A new high-sensitivity superconducting receiver for mm-wave remote sensing spectroscopy of the stratosphere, in *Ozone in the Troposphere and Stratosphere*, edited by R. D. Hudson, pp. 719–722, NASA, Greenbelt, MD, 1994a.
- de Zafra, R. L., L. K. Emmons, J. M. Reeves, and D. T. Shindell, An overview of millimeter-wave spectroscopic measurements of chlorine monoxide at Thule, Greenland, February–March, 1992: Vertical profiles, diurnal variation, and longer-term trends, *Geophys. Res. Lett.*, **21**, 1271–1274, 1994b.
- Dvortsov, V. L., S. G. Zvenigorodsky, and S. P. Smyslaev, On the use of Isaksen-Luther method of computing photodissociation rates in photochemical models, *J. Geophys. Res.*, **97**, 7593–7601, 1992.
- Froidevaux, L., M. Allen, and Y. L. Yung, A critical analysis of ClO and O₃ in the midlatitude stratosphere, *J. Geophys. Res.*, **90**, 12,999–13,030, 1985.
- Komhyr, W. D., R. D. Grass, R. D. Evans, R. K. Leonard, D. M. Quinby, D. J. Hofmann, and G. L. Koenig, Unprecedented 1993 ozone decrease over the United States from Dobson spectrophotometer observations, *Geophys. Res. Lett.*, **21**, 201–204, 1994.
- Manney, G. L., et al., Chemical depletion of ozone in the Arctic lower stratosphere during winter 1992–93, *Nature*, **370**, 429–434, 1994.
- Planet, W. G., J. H. Lienesch, A. J. Miller, R. Nagatani, R. D. McPeters, E. Hilsenrath, R. P. Cebula, M. T. DeLand, C. G. Wellemeyer, and K. Horvath, Northern hemisphere total ozone values from 1989–1993 determined with the NOAA-11 Solar Backscatter Ultraviolet (SBUV/2) instrument, *Geophys. Res. Lett.*, **21**, 205–208, 1994.
- Rodriguez, J. M., M. K. W. Ko, N. D. Sze, C. W. Heisey, G. K. Yue, and M. P. McCormick, Ozone response to enhanced heterogeneous processing after the eruption of Mt. Pinatubo, *Geophys. Res. Lett.*, **21**, 209–212, 1994.
- Rosen, J. M., N. T. Kjöme, H. Fast, and N. Larsen, Volcanic aerosol and polar stratospheric clouds in the winter 1992/93 north polar vortex, *Geophys. Res. Lett.*, **21**, 61–65, 1994.
- Solomon, S., Progress towards a quantitative understanding of Antarctic ozone depletion, *Nature*, **347**, 347–354, 1990.
- Stolarski, R., P. Bloomfield, R. McPeters, and J. Herman, Total ozone trends deduced from Nimbus 7 TOMS data, *Geophys. Res. Lett.*, **18**, 1015–1018, 1991.
- Tooney, D. W., J. G. Anderson, W. H. Brune, and K. R. Chan, In situ measurements of BrO in the Arctic stratosphere, *Geophys. Res. Lett.*, **17**, 513–516, 1990.
- Tooney, D. W., L. M. Avallone, L. R. Lait, P. A. Newman, M. R. Schoeberl, D. W. Fahey, E. L. Woodbridge, and J. G. Anderson, The seasonal evolution of reactive chlorine in the northern hemisphere stratosphere, *Science*, **261**, 1134–1136, 1993.
- Twomey, S., B. Herman, and R. Rabinoff, An extension of the Chahine method of inverting the radiative transfer equation, *J. Atmos. Sci.*, **34**, 1085–1090, 1977.
- Waters, J. W., L. Froidevaux, W. G. Read, G. L. Manney, L. S. Elson, D. A. Flower, R. F. Jarnot, and R. S. Harwood, Stratospheric ClO and ozone from the Microwave Limb

- Sounder on the Upper Atmospheric Research Satellite, *Nature*, 362, 597–602, 1993.
- Waters, J. W., G. L. Manney, W. G. Read, L. Froidevaux, D. A. Flower, and R. F. Jarnot, UARS MLS observations of lower stratospheric CIO in the 1992–93 and 1993–94 Arctic winter vortex, *Geophys. Res. Lett.*, in press, 1994.
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